

### **Detergents Containing Amylase and Percarboxylic Acid**

This invention relates to enzyme-containing detergents which, besides typical ingredients, contain an amylase from *Bacillus amyloliquefaciens* and a certain peroxidic bleaching agent.

Besides the ingredients essential to the washing process, such as surfactants and builders, detergents generally contain other ingredients which may be collectively referred to as washing aids and which comprise such different groups of ingredients as foam regulators, redeposition inhibitors, bleaching agents, bleach activators and dye transfer inhibitors. The washing aids in question also include substances which support cleaning performance through the enzymatic degradation of soils present on the fabric. The same also applies to detergents for cleaning hard surfaces. Besides the proteases which assist in removing proteins and the lipolytic lipases, particular significance attaches to the amylases, of which the function is to facilitate the removal of starch-containing soils through the catalytic hydrolysis of the starch polysaccharide and which have long been used for this purpose in dishwashing detergents and also in laundry detergents. Hitherto by far the most predominant amylase has been a heat-stable amylase from *Bacillus licheniformis* which is commercially obtainable, for example, as Termamyl®. More recently, genetically modified amylases, i.e. amylases with an amino acid sequence modified by genetic methods by comparison with naturally occurring amylases, have been used in detergents. Besides increasing their performance, the main object of genetically modifying amylases is to increase the stability of the enzyme, more particularly against attack by oxidizing agents. One way of achieving this goal, which was proposed in International patent application WO 94/18314, is to remove amino acids particularly susceptible to oxidation, such as methionine, tryptophane, cysteine or tyrosine, from the

amino acid sequence of the amylase or to replace them with other amino acids more stable to oxidation. A similar approach is also proposed in International patent application **WO 95/21247** which recommends replacing at least one methionine in the amylase amino acid sequence by an amino acid which is neither methionine nor cysteine.

Although such genetic modifications can lead to improved amylase stability under certain conditions of use, they do not help towards increasing the contribution of the amylase to the cleaning performance of corresponding detergents in which the amylase is present.

It has now surprisingly been found that the combination of a naturally occurring  $\alpha$ -amylase with a certain peroxidic oxidizing agent leads to unexpected synergistic improvements in performance when used in detergents.

Accordingly, the present invention relates to an amylase-containing detergent which contains  $\alpha$ -amylase from *Bacillus amyloliquefaciens* and a percarboxylic acid and/or an alkali metal salt thereof in addition to typical ingredients compatible with such components.

The present invention also relates to the use of a corresponding combination for increasing the cleaning performance of detergents, more particularly against starch-containing and/or colored soils, when used in wash liquors, more particularly water-containing wash liquors. The cleaning performance against colored soils is meant to be interpreted in its broadest sense and encompasses both the bleaching of soil on the textile, the bleaching of soil detached from the textile in the wash liquor and the oxidative destruction in the wash liquor of textile dyes detached from textiles under the washing conditions before they can be absorbed onto textiles of another color. Where the combination according to the invention is used in cleaning solutions for hard surfaces, the expression "cleaning performance" is likewise intended to encompass the bleaching of soil,

especially tea, on the hard surface and the bleaching of soil detached from the hard surface in the dishwashing liquor.

$\alpha$ -Amylase from *Bacillus amyloliquefaciens* has been known for some time, for example from US Patent **US 1,227,374**, and is commercially obtainable, for example, as Amylase BAN®.

A detergent according to the invention preferably contains 0.001 mg to 0.5 mg and, more particularly, 0.02 mg to 0.3 mg of amylolytic protein per gram of the detergent as a whole. The protein concentration may be determined by known methods, for example by the bicinchoninic acid process (BCA process, Pierce Chemical Co., Rockford, IL.) or by the biuret process (A.G. Gornall, C.S. Bardawill and M.M. David, *J. Biol. Chem.* **177**, 751-766, 1948).

A detergent according to the invention preferably contains 0.5% by weight to 20% by weight and more particularly 1% by weight to 15% by weight of percarboxylic acid, the term percarboxylic acid being intended to encompass both the free acid and the percarboxylic acid salts, more particularly the alkali metal salts. Both aliphatic percarboxylic acids and aromatic percarboxylic acids such as, for example, perbenzoic acid or perphthalic acid may be used. The percarboxylic acid is preferably selected from compounds corresponding to general formula (I):



in which n is a number of 8 to 20 and more particularly 10 to 14, or from amidoalkylpercarboxylic acids, more particularly phthalimidoalkyl percarboxylic acids. In the last-mentioned case, phthalimidopercaproic acid is particularly preferred. Among the dipercarboxylic acids corresponding to formula I, 1,12-diperdodecanedioic acid and 1,9-diperazelaic acid are particularly preferred.

Amidoalkyl percarboxylic acids and their production are known, for example, from European patent applications **EP 0 349 940** and **EP 0 739 880**.

The percarboxylic acids may be incorporated in detergents, 5 particularly in solid detergents, according to the invention in optionally compounded or coated foam, as known for example from European patents **EP 0 450 587**, **EP 0 521 962**, **EP 0 695 343** or European patent application **EP 0 816 418**.

Besides the active-substance combination used in accordance with 10 the invention, the detergents according to the invention - which may be present as, in particular, powder-form solids, as post-compacted particles or as homogeneous solutions or suspensions - may in principle contain any known ingredients typically encountered in detergents. More particularly, the detergents according to the invention may contain builders, surfactants, 15 additional bleaching agents based on organic and/or inorganic peroxygen compounds, bleach activators, water-miscible organic solvents, additional enzymes, sequestering agents, electrolytes, pH regulators and other auxiliaries, such as optical brighteners, redeposition inhibitors, dye transfer inhibitors, foam regulators, silver corrosion inhibitors and dyes and 20 perfumes.

The detergents according to the invention may contain one or more surfactants, more particularly anionic surfactants, nonionic surfactants and mixtures thereof, but also cationic, zwitterionic and amphoteric surfactants.

Suitable nonionic surfactants are, in particular, alkyl glycosides and 25 ethoxylation and/or propoxylation products of alkyl glycosides or linear or branched alcohols containing 12 to 18 carbon atoms in the alkyl moiety and 3 to 20 and preferably 4 to 10 alkyl ether groups. Corresponding ethoxylation and/or propoxylation products of N-alkylamines, vicinal diols, fatty acid esters and fatty acid amides, which correspond to the long-chain 30 alcohol derivatives mentioned in regard to the alkyl moiety, and of alkyl

phenols containing 5 to 12 carbon atoms in the alkyl group are also suitable.

Preferred nonionic surfactants are alkoxylated, advantageously ethoxylated, more particularly primary alcohols preferably containing 8 to 5 18 carbon atoms and an average of 1 to 12 moles of ethylene oxide (EO) per mole of alcohol, in which the alcohol group may be linear or, preferably, 2-methyl-branched or may contain linear and methyl-branched groups in the form of the mixtures typically present in oxoalcohol groups. However, alcohol ethoxylates containing linear groups of alcohols of native origin with 10 12 to 18 carbon atoms, for example coconut alcohol, palm alcohol, tallow alcohol or oleyl alcohol, and an average of 2 to 8 EO per mole of alcohol are particularly preferred. Preferred ethoxylated alcohols include, for example, C<sub>12-14</sub> alcohols containing 3 EO or 4 EO, C<sub>9-11</sub> alcohols containing 7 EO, C<sub>13-15</sub> alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C<sub>12-18</sub> alcohols 15 containing 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C<sub>12-14</sub> alcohol containing 3 EO and C<sub>12-18</sub> alcohol containing 7 EO. The degrees of ethoxylation mentioned are statistical mean values which, for a special product, may be either a whole number or a broken number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow 20 range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols containing more than 12 EO may also be used. Examples of such fatty alcohols are (tallow) fatty alcohols containing 14 EO, 16EO, 20EO, 25 EO, 30 EO or 40 EO. In dishwasher detergents in particular, extremely low-foaming surfactants are normally used. These preferably include 25 C<sub>12-18</sub> alkyl polyethylene glycol polypropylene glycol ethers containing up to 8 moles ethylene oxide and up to 8 moles propylene oxide units in the molecule. However, other known low-foaming nonionic surfactants, for example C<sub>12-18</sub> alkyl polyethylene glycol polybutylene glycol ethers containing up to 8 moles ethylene oxide and up to 8 moles butylene oxide

units in the molecule and end-capped alkyl polyalkylene glycol mixed ethers, may also be used. The hydroxyfunctional alkoxylated alcohols described in European patent application EP 0 300 305, so-called hydroxy mixed ethers, are also particularly preferred. The nonionic surfactants also 5 include alkyl glycosides with the general formula RO(G)<sub>x</sub> where R is a primary, linear or methyl-branched, more particularly 2-methyl-branched, aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G is a glucose unit containing 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization x, which indicates the distribution of mono- 10 and oligoglycosides, is a number (which, as an analytically determined quantity, may also be a broken number) of 1 to 10; preferably x = 1.2 to 1.4. Other suitable nonionic surfactants are polyhydroxyfatty acid amides corresponding to formula (II):



in which R<sup>1</sup>CO is an aliphatic acyl group containing 6 to 22 carbon atoms, 20 R<sup>2</sup> is hydrogen, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl group containing 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxyfatty acid amides are preferably derived from reducing sugars containing 5 or 6 carbon atoms, more particularly from glucose. The group of polyhydroxy- 25 fatty acid amides also includes compounds corresponding to formula (III):



in which R<sup>3</sup> is a linear or branched alkyl or alkenyl group containing 7 to 12 carbon atoms, R<sup>4</sup> is a linear, branched or cyclic alkylene group or an

arylene group containing 2 to 8 carbon atoms and R<sup>5</sup> is a linear, branched or cyclic alkyl group or an aryl group or a hydroxyalkyl group containing 1 to 8 carbon atoms, C<sub>1-4</sub> alkyl or phenyl groups being preferred, and [Z] is a linear polyhydroxyalkyl group, of which the alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of such a group. Again, [Z] is preferably obtained by reductive amination of a sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy or N-aryloxy-substituted compounds may then be converted into the required polyhydroxyfatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example in accordance with the teaching of International patent application **WO-A-95/07331**. Another class of preferred nonionic surfactants which are used either as sole nonionic surfactant or in combination with other nonionic surfactants, particularly together with alkoxylated fatty alcohols and/or alkyl glycosides, are alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters preferably containing 1 to 4 carbon atoms in the alkyl chain, more particularly the fatty acid methyl esters which are described, for example, in Japanese patent application **JP 58/217598** or which are preferably produced by the process described in International patent application **WO 90/13533**. Nonionic surfactants of the amine oxide type, for example N-coconutalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethyl amine oxide, and the fatty acid alkanolamide type are also suitable. The quantity in which these nonionic surfactants are used is preferably no more, in particular no more than half, the quantity of ethoxylated fatty alcohols used. Other suitable surfactants are so-called gemini surfactants. Gemini surfactants are generally understood to be compounds which contain two hydrophilic groups and two hydrophobic groups per molecule. These groups are generally separated from one another by a so-called Aspacer. The spacer is generally a carbon chain

which should be long enough for the hydrophilic groups to have a sufficient spacing to be able to act independently of one another. Gemini surfactants are generally distinguished by an unusually low critical micelle concentration and by an ability to reduce the surface tension of water to a considerable extent. In exceptional cases, however, gemini surfactants are not only understood to be "dimeric" surfactants, but also "trimeric" surfactants. Suitable gemini surfactants are, for example, the sulfated hydroxy mixed ethers according to German patent application **DE 43 21 022** and the dimer alcohol bis- and trimer alcohol tris-sulfates and -ether sulfates according to German patent application **DE 195 03 061**. The end-capped dimeric and trimeric mixed ethers according to German patent application **DE 195 13 391** are distinguished in particular by their bifunctionality and multifunctionality. Thus, the end-capped surfactants mentioned exhibit good wetting properties and are low-foaming so that they are particularly suitable for use in machine washing or cleaning processes. However, the gemini polyhydroxyfatty amides or poly-polyhydroxyfatty acid amides described in International patent applications **WO 95/19953**, **WO 95/19954** and **WO 95/19955** may also be used.

Suitable anionic surfactants are in particular soaps and those containing sulfate or sulfonate groups. Suitable surfactants of the sulfonate type are preferably C<sub>9-13</sub> alkyl benzenesulfonates, olefin sulfonates, i.e. mixtures of alkene and hydroxyalkane sulfonates, and the disulfonates obtained, for example, from C<sub>12-18</sub> monoolefins with an internal or terminal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Other suitable surfactants of the sulfonate type are the alkane sulfonates obtained from C<sub>12-18</sub> alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization. The esters of  $\alpha$ -sulfofatty acids (ester sulfonates), for example the  $\alpha$ -sulfonated methyl esters of hydrogenated coconut, palm

kernel or tallow acids, which are obtained by  $\alpha$ -sulfonation of the methyl esters of fatty acids of vegetable and/or animal origin containing 8 to 20 carbon atoms in the fatty acid molecule and subsequent neutralization to water-soluble monosalts are also suitable. The esters in question are 5 preferably the  $\alpha$ -sulfonated esters of hydrogenated coconut, palm, palm kernel or tallow acid, although sulfonation products of unsaturated fatty acids, for example oleic acid, may also be present in small quantities, preferably in quantities of not more than about 2 to 3% by weight.  $\alpha$ -Sulfofatty acid alkyl esters with an alkyl chain of not more than 4 carbon 10 atoms in the ester group, for example methyl esters, ethyl esters, propyl esters and butyl esters, are particularly preferred. The methyl esters of  $\alpha$ -sulfofatty acids (MES) and saponified disalts thereof are used with particular advantage. Other suitable anionic surfactants are sulfonated fatty acid glycerol esters, i.e. the monoesters, diesters and triesters and 15 mixtures thereof which are obtained where production is carried out by esterification of a monoglycerol with 1 to 3 moles of fatty acid or in the transesterification of triglycerides with 0.3 to 2 moles of glycerol. Preferred alk(en)yl sulfates are the alkali metal salts and, in particular, the sodium salts of the sulfuric acid semiesters of C<sub>12-18</sub> fatty alcohols, for example 20 cocofatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or C<sub>10-20</sub> oxoalcohols and the corresponding semiesters of secondary alcohols with the same chain length. Other preferred alk(en)yl sulfates are those with the chain length mentioned which contain a synthetic, linear alkyl chain based on a petrochemical and which are similar 25 in their degradation behavior to the corresponding compounds based on oleochemical raw materials. C<sub>12-16</sub> alkyl sulfates and C<sub>12-15</sub> alkyl sulfates and also C<sub>14-15</sub> alkyl sulfates are particularly preferred from the washing performance point of view. Other suitable anionic surfactants are 2,3-alkyl sulfates which may be produced, for example, in accordance with **US**

**3,234,258** or **US 5,075,041** and which are commercially obtainable as products of the Shell Oil Company under the name of DAN®. The sulfuric acid monoesters of linear or branched C<sub>7-21</sub> alcohols ethoxylated with 1 to 6 moles of ethylene oxide, such as 2-methyl-branched C<sub>9-11</sub> alcohols 5 containing on average 3.5 moles of ethylene oxide (EO) or C<sub>12-18</sub> fatty alcohols containing 1 to 4 EO, are also suitable. Other preferred anionic surfactants are the salts of alkyl sulfosuccinic acid which are also known as sulfosuccinates or as sulfosuccinic acid esters and which represent monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably 10 fatty alcohols and, more particularly, ethoxylated fatty alcohols. Preferred sulfosuccinates contain C<sub>8-18</sub> fatty alcohol molecules or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol molecule derived from ethoxylated fatty alcohols which, considered in isolation, represent nonionic surfactants. Of these sulfosuccinates, those of which 15 the fatty alcohol molecules are derived from narrow-range ethoxylated fatty alcohols are particularly preferred. Alk(en)yl succinic acid preferably containing 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof may also be used. Other suitable anionic surfactants are fatty acid derivatives of amino acids, for example of N-methyl taurine (taurides) and/or of N- 20 methyl glycine (sarcosides). The sarcosides or rather sarcosinates, above all sarcosinates of higher and optionally mono- or poly-unsaturated fatty acids, such as oleyl sarcosinate, are particularly preferred. Other suitable anionic surfactants are, in particular, soaps. Suitable soaps are, in particular, saturated fatty acid soaps, such as the salts of lauric acid, 25 myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and soap mixtures derived in particular from natural fatty acids, for example coconut, palm kernel or tallow acids. The known alkenyl succinic acid salts may be used together with or as a substitute for soaps.

The anionic surfactants, including the soaps, may be present in the 30 form of their sodium, potassium or ammonium salts and as soluble salts of

organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably present in the form of their sodium or potassium salts and, more preferably, in the form of their sodium salts.

Surfactants are present in laundry detergents according to the invention in quantities of preferably 5% by weight to 50% by weight and more preferably in quantities of 8% by weight to 30% by weight whereas detergents for cleaning hard surfaces, particularly dishwasher detergents, have lower surfactant contents of up to 10% by weight, preferably up to 5% by weight and more preferably in the range from 0.5% by weight to 3% by weight.

A detergent according to the invention preferably contains at least one water-soluble and/or water-insoluble, organic and/or inorganic builder. Suitable water-soluble organic builders include polycarboxylic acids, more particularly citric acid and sugar acids, monomeric and polymeric aminopolycarboxylic acids, more particularly methyl glycine diacetic acid, nitrilotriacetic acid and ethylenediamine tetraacetic acid and polyaspartic acid, polyphosphonic acids, more especially aminotris(methylene phosphonic acid), ethylenediamine tetrakis(methylene phosphonic acid) and 1-hydroxyethane-1,1-diphosphonic acid, polymeric hydroxy compounds, such as dextrin, and polymeric (poly)carboxylic acids, more particularly the polycarboxylates obtainable by oxidation of polysaccharides or dextrans according to European patent **0 625 992** or International patent application **WO 92/18542** or European patent **EP 0 232 202**, polymeric acrylic acids, methacrylic acids, maleic acids and copolymers thereof which may also contain small amounts of polymerizable substances with no carboxylic acid functionality in copolymerized form. The relative molecular weight of the homopolymers of unsaturated carboxylic acids is generally between 3,000 and 200,000 while the relative molecular weight of the copolymers is between 2,000 and 200,000 and preferably between 30,000 and 120,000, based on free acid. A particularly preferred acrylic

acid/maleic acid copolymer has a relative molecular weight of 30,000 to 100,000. Commercial products are, for example, Sokalan® CP 5, CP 10 and PA 30 of BASF. Suitable, but less preferred, compounds of this class are copolymers of acrylic acid or methacrylic acid with vinyl ethers, such as

5      vinyl methyl ethers, vinyl esters, ethylene, propylene and styrene, in which the acid makes up at least 50% by weight. Other suitable water-soluble organic builders are terpolymers which contain two unsaturated acids and/or salts thereof as monomers and vinyl alcohol and/or an esterified vinyl alcohol or a carbohydrate as the third monomer. The first acidic

10     monomer or its salt is derived from a monoethylenically unsaturated C<sub>3-8</sub> carboxylic acid and preferably from a C<sub>3-4</sub> monocarboxylic acid, more especially (meth)acrylic acid. The second acidic monomer or its salt may be a derivative of a C<sub>4-8</sub> dicarboxylic acid, maleic acid being particularly preferred, and/or a derivative of an allylsulfonic acid substituted in the 2-

15     position by an alkyl or aryl group. Polymers such as these can be produced in particular by the processes described in German patents **DE 42 21 381** and German patent application **DE 43 00 772** and generally have a relative molecular weight of 1,000 to 200,000. Other preferred copolymers are the copolymers which are described in German patent

20     applications **DE 43 03 320** and **DE 44 17 734** and which preferably contain acrolein and acrylic acid/acrylic acid salts or vinyl acetate as monomers. The organic builders may advantageously be used in the form of aqueous solutions, preferably in the form of 30 to 50% by weight aqueous solutions, particularly for the production of liquid detergents. All the acids mentioned

25     are generally used in the form of their water-soluble salts, more especially their alkali metal salts.

If desired, organic builders of the type in question may be present in quantities of up to 40% by weight, preferably in quantities of up to 25% by weight and more preferably in quantities of 1% by weight to 8% by weight.

30     Quantities near the upper limit are preferably used in paste-form or liquid,

more particularly water-containing detergents.

Suitable water-soluble inorganic builders are, in particular, alkali metal silicates, alkali metal carbonates and alkali metal phosphates which may be present in the form of their alkaline, neutral or acidic sodium or potassium salts. Examples of such builders are trisodium phosphate, 5 tetrasodium diphosphate, disodium dihydrogen diphosphate, pentasodium triphosphate, so-called sodium hexametaphosphate, oligomeric trisodium phosphate with degrees of oligomerization of 5 to 1,000 and more particularly 5 to 50 and the corresponding potassium salts or mixtures of 10 sodium and potassium salts. Crystalline or amorphous alkali metal aluminosilicates in quantities of up to 50% by weight and preferably not more than 40% by weight and, in liquid detergents in particular, in quantities of 1 to 5% by weight are used as water-insoluble, water-dispersible inorganic builder materials. Of these inorganic builders, crystalline sodium 15 aluminosilicates in detergent quality, more particularly zeolite A, P and optionally X, individually or in the form of mixtures, for example in the form of a co-crystallize of the zeolites A and X (Vegobond® AX, a product of Condea Augusta S.P.A.), are preferred. Quantities near the upper limit mentioned are preferably used in solid particulate detergents. Suitable 20 aluminosilicates contain no particles larger than 30 µm in size, at least 80% by weight preferably consisting of particles smaller than 10 µm in size. Their calcium binding capacity, which may be determined in accordance with German patent DE 24 12 837, is generally in the range from 100 to 200 mg CaO per gram.

25        Suitable substitutes or partial substitutes for the aluminosilicate mentioned are crystalline alkali metal silicates which may be present either on their own or in the form of a mixture with amorphous silicates. The alkali metal silicates suitable as builders in the detergents according to the invention preferably have a molar ratio of alkali metal oxide to SiO<sub>2</sub> of less than 0.95:1 and, more particularly, in the range from 1:1.1 to 1:12 and may 30

be amorphous or crystalline. Preferred alkali metal silicates are sodium silicates, more especially amorphous sodium silicates, with a molar Na<sub>2</sub>O : SiO<sub>2</sub> ratio of 1:2 to 1:2.8. Those with a molar Na<sub>2</sub>O : SiO<sub>2</sub> ratio of 1:1.9 to 1:2.8 can be produced by the method according to European patent application **EP 0 425 427**. Crystalline layer silicates with the general formula Na<sub>2</sub>Si<sub>x</sub>O<sub>2x+1</sub> · y H<sub>2</sub>O, in which x – the so-called modulus – is a number of 1.9 to 22 and more particularly 1.9 to 4 and y is a number of 0 to 33, preferred values for x being 2, 3 or 4, are preferably used as crystalline silicates which may be present either on their own or in admixture with amorphous silicates. Crystalline layer silicates which correspond to this general formula are described, for example, in European patent application **EP 0 164 514**. Preferred crystalline layer silicates are those in which x in the general formula shown above assumes a value of 2 or 3. Both  $\exists$ - and \*-sodium disilicates (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> · yH<sub>2</sub>O) are particularly preferred,  $\exists$ -sodium disilicate being obtainable for example by the process described in International patent application **WO 91/08171**. \*-Sodium silicates with a modulus of 1.9 to 3.2 may be produced in accordance with Japanese patent applications **JP 04/238 809** or **JP 04/260 610**. Substantially water-free crystalline alkali metal silicates corresponding to the above general formula, in which x is a number of 1.9 to 2.1, obtainable from amorphous alkali metal silicates as described in European patent applications **EP 0 548 599**, **EP 0 502 325** and **EP 0 425 428** may also be used in detergents according to the invention. Another preferred embodiment of the detergents according to the invention is characterized by the use of a crystalline sodium layer silicate with a modulus of 2 to 3 which may be produced from sand and soda by the process according European patent application **EP 0 436 835**. The crystalline sodium silicates with a modulus of 1.9 to 3.5 which may be obtained by the processes according to European patents **EP 0 164 552** and/or **EP 0 294 753** are used in a

another preferred embodiment of the detergents according to the invention. Crystalline layer silicates corresponding to formula (I) are marketed, for example, by Clariant GmbH under the trade name Na-SKS, including for example Na-SKS-1 ( $\text{Na}_2\text{Si}_{22}\text{O}_{45} \cdot x\text{H}_2\text{O}$ , kenyaite) Na-SKS-2 (5  $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ , magadiite), Na-SKS-3 ( $\text{Na}_2\text{Si}_8\text{O}_{17} \cdot x\text{H}_2\text{O}$ ), Na-SKS-4 ( $\text{Na}_2\text{Si}_4\text{O}_9 \cdot x\text{H}_2\text{O}$ , makatite). Of these, Na-SKS-5 ( $\forall\text{-Na}_2\text{Si}_2\text{O}_5$ ), Na-SKS-7 ( $\exists\text{-Na}_2\text{Si}_2\text{O}_5$  natrosilite), Na-SKS-9 ( $\text{NaHSi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ), Na-SKS-10 (10  $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , kanemite), Na-SKS-11 ( $9\text{-Na}_2\text{Si}_2\text{O}_5$ ) and Na-SKS-13 ( $\text{NaHSi}_2\text{O}_5$ ), but especially Na-SKS-6 ( $*\text{-Na}_2\text{Si}_2\text{O}_5$ ), are particularly 15 suitable. An overview of crystalline layer silicates can be found, for example, in the articles published in "**Hoechst High Chem Magazin 14/1993**", pages 33-38 and in "**"Seifen-Öle-Fette-Wachse"**", Vol. 116, No. 20/1990", pages 805-808. Another preferred embodiment of the detergents according to the invention is characterized by the use of the 15 granular compound of crystalline layered silicate and citrate, of crystalline layered silicate and the above-mentioned (co)polymeric polycarboxylic acid, as described for example in German patent application **DE 198 19 187**, or of alkali metal silicate and alkali metal carbonate, as described, for example, in International patent application **WO 95/22592** or as 20 commercially obtainable, for example, under the name of Nabion® 15.

Builders may optionally be present in the detergents according to the invention in quantities of up to 90% by weight and are preferably present in quantities of up to 75% by weight. Laundry detergents according to the invention have builder contents of, in particular, 5% by weight to 50% by 25 weight. In hard-surface cleaning compositions, more particularly dishwasher detergents, according to the invention, the builder content is in particular between 5% by weight and 88% by weight, such compositions preferably being free from water-insoluble builders. Another preferred embodiment of the dishwasher detergents according to the invention

contains 20% by weight to 40% by weight of a water-soluble organic builder, more particularly alkali metal citrate, 3% by weight to 15% by weight of alkali metal carbonate and 20% by weight to 40% by weight of alkali metal disilicate.

5        Additional peroxygen compounds suitable for use in detergents according to the invention include, in particular, hydrogen peroxide and inorganic salts which release hydrogen peroxide under washing conditions, including perborate, percarbonate, persilicate and/or persulfate, such as caroate. If solid peroxygen compounds are to be used, they may be used  
10      in the form of powders or granules which may even be coated in known manner. The addition of small quantities of known bleach stabilizers, for example phosphonates, borates or metaborates and metasilicates, and magnesium salts, such as magnesium sulfate, can be useful.

The bleach activators used may be compounds which form aliphatic  
15      peroxocarboxylic acids containing preferably 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions. Substances bearing O- and/or N-acyl groups with the number of carbon atoms mentioned and/or optionally substituted benzoyl groups are suitable. Preferred bleach  
20      activators are polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, more particularly tetraacetyl glycoluril (TAGU), N-acylimides, more particularly N-nanonoyl succinimide (NOSI), acylated phenol sulfonates,  
25      more particularly n-nanonoyl- or isanonanoyl-oxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more particularly phthalic anhydride, acylated polyhydric alcohols, more particularly triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from German patent applications **DE 196 16 693** and **DE 196 16 767**, acetylated  
30      sorbitol and mannitol and the mixtures thereof (SORMAN) described in

European patent application **EP 0 525 239**, acylated sugar derivatives, more particularly pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example N-benzoyl caprolactam, which are known from International patent applications **WO 94/27970**, **WO 94/28102**, **WO 94/28103**, **WO 95/00626**, **WO 95/14759** and **WO 95/17498**. The substituted hydrophilic acyl acetals known from German patent application **DE 196 16 769** and the acyl lactams described in German patent application **DE 196 16 770** and in International patent application **WO 95/14075** are also preferably used. The combinations of conventional bleach activators known from German patent application **DE 44 43 177** may also be used. Where the above-mentioned bleaching agents yielding hydrogen peroxide are present, bleach activators such as these are present in the usual quantities, preferably in quantities of 0.5% by weight to 10% by weight and more preferably in quantities of 1% by weight to 8% by weight, based on the detergent as a whole, but are preferably absent altogether where the percarboxylic acid crucial to the invention is used

In addition to or instead of the conventional bleach activators mentioned above, the sulfonimines known from European patents **EP 0 446 982** and **EP 0 453 003** and/or bleach-boosting transition metal salts or transition metal complexes may also be present as so-called bleach catalysts.

Enzymes suitable for use in the detergents according to the invention in addition to the amylase crucial to the invention are those from the class of proteases, lipases, cutinases, pullulanases, hemicellulases, cellulases, oxidases, laccases and peroxidases and mixtures thereof. Other amylases than the amylase crucial to the invention may also be present in addition to that amylase. Enzymes obtained from fungi or bacteria, such as *Bacillus subtilis*, *Bacillus licheniformis*, *Bacillus lentus*,

Streptomyces griseus, Humicola lanuginosa, Humicola insolens, Pseudomonas peudoalcaligenes, Pseudomonas cepacia and Coprinus cinereus are particularly suitable. The amylase crucial to the invention and the enzymes optionally used in addition may be adsorbed to supports 5 and/or embedded in membrane materials to protect them against premature inactivation, as described for example in European patent EP 0 564 476 or in International patent application **WO 94/23005**. They are present in the detergents according to the invention in quantities of preferably up to 5% by weight and, more preferably, 0.2% by weight to 2% 10 by weight. If the detergent according to the invention contains protease, it preferably has a proteolytic activity of about 100 PU/g to about 10,00 PU/g and more particularly in the range from 300 PU/g to 8,000 PU/g. If several enzymes are to be used in the detergent according to the invention, this may be done by incorporating the two or more separate enzymes or the 15 two or more enzymes separately compounded in known manner or two or more enzymes compounded together in the form of granules, as known for example from International patent applications **WO 96/00772** or **WO 96/00773**.

The organic solvents suitable for use besides water in the 20 detergents according to the invention, particularly where they are present in liquid or paste-like form, include C<sub>1-4</sub> alcohols, more especially methanol, ethanol, isopropanol and tert. butanol, C<sub>2-4</sub> diols, more especially ethylene glycol and propylene glycol, and mixtures thereof and ethers derived from the classes of compound mentioned. Water-miscible solvents such as 25 these are present in the detergents according to the invention in quantities of preferably not more than 30% by weight and, more preferably, between 6% by weight and 20% by weight.

The detergents may additionally contain other typical detergent ingredients. These optional constituents include, in particular, enzyme 30 stabilizers, redeposition inhibitors, dye transfer inhibitors, foam inhibitors

and optical brighteners and also dyes and perfumes. To protect silverware against corrosion, dishwasher detergents according to the invention may contain silver corrosion inhibitors. In addition, a hard-surface detergent according to the invention may contain abrasive ingredients, more 5 especially from the group consisting of silica flours, wood flours, polymer powders, chalks and glass microbeads and mixtures thereof. Abrasives are present in the dishwasher detergents according to the invention in quantities of preferably not more than 20% by weight and, more particularly, in quantities of 5% by weight to 15% by weight.

10 To establish a desired pH value which is not spontaneously adjusted by the mixture of the other components, the detergents according to the invention may contain system-compatible and environmentally compatible acids, more particularly citric acid, acetic acid, tartaric acid, malic acid, lactic acid, glycolic acid, succinic acid, glutaric acid and/or adipic acid and 15 also mineral acids, more especially sulfuric acid, or bases, more especially ammonium or alkali metal hydroxides. pH regulators such as these are present in the detergents according to the invention in quantities of preferably not more than 20% by weight and, more preferably, between 1.2% by weight and 17% by weight.

20 Dye transfer inhibitors suitable for use in laundry detergents according to the invention include, in particular, polyvinyl pyrrolidones, polyvinyl imidazoles, polymeric N-oxides, such as poly-(vinylpyridine-N-oxide) and copolymers of vinyl pyrrolidone with vinyl imidazole.

The function of redeposition inhibitors is to keep the soil detached 25 from the fibers suspended in the wash liquor. Suitable redeposition inhibitors are water-soluble, generally organic colloids, for example starch, glue, gelatine, salts of ether carboxylic acids or ether sulfonic acids of starch or cellulose or salts of acidic sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acidic groups are also 30 suitable for this purpose. Other starch products than the starch derivatives

mentioned above, for example aldehyde starches, may also be used. Cellulose ethers, such as carboxymethyl cellulose (sodium salt), methyl cellulose, hydroxyalkyl cellulose, and mixed ethers, such as methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, methyl 5 carboxymethyl cellulose and mixtures thereof, are also preferably used, for example in quantities of 0.1 to 5% by weight, based on the detergent.

Laundry detergents according to the invention may contain derivatives of diaminostilbene disulfonic acid or alkali metal salts thereof as optical brighteners. Suitable optical brighteners are, for example, salts of 10 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar structure which contain a diethanolamino group, a methylamino group and anilino group or a 2-methoxyethylamino group instead of the morpholino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'- 15 bis-(2-sulfostyryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostyryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned may also be used.

Particularly where the detergents are used in washing machines, it can be of advantage to add typical foam inhibitors to them. Suitable foam 20 inhibitors are, for example, soaps of natural or synthetic origin which have a high percentage content of C<sub>18-24</sub> fatty acids. Suitable non-surface-active foam inhibitors are, for example, organopolysiloxanes and mixtures thereof with microfine, optionally silanized, silica and also paraffins, waxes, microcrystalline waxes and mixtures thereof with silanized silica or bis- 25 stearyl ethylenediamide. Mixtures of different foam inhibitors, for example mixtures of silicones, paraffins and waxes, may also be used with advantage. The foam inhibitors, more particularly silicone- and/or paraffin-containing foam inhibitors, are preferably fixed to a granular water-soluble or water-dispersible support. Mixtures of paraffins and bis-stearyl 30 ethylenediamides are particularly preferred.

The production of solid detergents according to the invention does not involve any difficulties and may be carried out in known manner, for example by spray drying or granulation, the enzymes and any other heat-sensitive ingredients, for example bleaching agents, optionally being 5 separately added at a later stage. Detergents according to the invention having a high bulk density, more particularly in the range from 650 to 950 g/l, are preferably produced by the process comprising an extrusion step which is known from European patent **EP 0 486 592**. Another preferred production process is the granulation process according to European 10 patent **EP 0 642 576**.

To produce detergents according to the invention in the form of tablets which comprise one or more phases and are colored in one or more colors and, in particular, may consist of one layer or several layers, more particularly two layers, all the ingredients - optionally for each layer - may 15 be mixed together in a mixer and the resulting mixture tabletted in conventional tablet presses, for example eccentric presses or rotary presses, under pressures of about 50 to 100 kN and preferably under pressures of 60 to 70 kN. In the case of multilayer tablets in particular, it can be of advantage if at least one layer is compressed in advance. In the case of 20 multilayer tablets in particular, it can be of advantage if at least one layer is compressed in advance, preferably under pressures of 5 to 20 kN and more particularly 10 to 15 kN. Fracture-resistant tablets which still dissolve sufficiently quickly under in-use conditions are readily obtained in this way; they have fracture and flexural strengths of normally 100 to 200 N and 25 preferably above 150 N. A tablet produced in this way preferably has a weight of 10 g to 50 g and, more particularly, 15 g to 40 g. The tablets may be of any shape, including round, oval or angular and variations thereof. Corners and edges are advantageously rounded off. Round tablets preferably have a diameter of 30 mm to 40 mm. The size of rectangular or 30 square tablets in particular, which are mainly introduced from dispensing

compartments, for example of dishwashers, is dependent on the geometry and the size of the dispensing compartment. For example, preferred embodiments have a base area of (20 to 30 mm) x (34 to 40 mm) and, more particularly, 26 x 36 mm or 24 x 38 mm.

5       Liquid or paste-form detergents according to the invention in the form of solutions containing typical solvents are generally prepared simply by mixing the ingredients which may be introduced into an automatic mixer either as such or in the form of a solution.

### **Examples**

10    Example 1

To determine washing performance, cotton fabric soiled with standardized test soils was washed in a domestic washing machine (Miele® W 701) at 40°C (detergent dose 76 g, water hardness 16°d, load 3.5 kg, short program). The washing tests were carried out with a 15 detergent **C1** containing 0.25% by weight of known amylase granules (Termamyl® 60T) and 0.25% by weight of protease granules (activity 200,000 PU/g) with the *Bacillus latus* protease and 4% by weight of 1,12-diperdodecanedioic acid; a detergent **C2** which instead of Termamyl® contained the protein-equivalent quantity of the genetically modified 20 amylase Duramyl® for otherwise the same composition as **C1**; a detergent **C3** which instead of Termamyl® contained the protein-equivalent quantity of the genetically modified amylase Purafect® OxAm for otherwise the same composition as **C1**; a detergent **C4** which instead of Termamyl® contained the protein-equivalent quantity of the fungal amylase Fungamyl® 25 for otherwise the same composition as **C1**; a detergent **D1** according to the invention which instead of Termamyl® contained the protein-equivalent quantity of amylase from *Bacillus amyloliquefaciens* for otherwise the same composition as **C1** and a detergent **D2** according to the invention which instead of 1,12-diperdodecanedionic acid contained the same quantity of 30 phthalimidopercaproic acid for otherwise the same composition as **D1**.

The detergents according to the invention were distinctly superior in their washing performance to the detergents containing another amylase. The outcome was largely the same when the per acid in the detergents according to the invention was replaced by a conventional bleaching system of perborate/TAED.

Example 2

Dishwasher detergents **C5** and **C6** containing 55% by weight of sodium tripolyphosphate (counted as water-free), 4% by weight of amorphous sodium disilicate (counted as water-free), 22% by weight of sodium carbonate, 11% by weight of phthalimidopercaproic acid, 2% by weight of nonionic surfactant and 1% by weight or 2% by weight of amylase granules (Termamyl® 60T) and 1.4% by weight of protease granules (activity 200,000 PU/g) with the *Bacillus latus* protease (balance to 100% by weight water, perfume and dye), **C7** and **C8** which instead of Termamyl® contained protein-equivalent quantities of Duramyl® for otherwise the same composition as **C5** and **C6**, and **M3** and **M4** according to the invention which instead of Termamyl® contained protein-equivalent quantities of amylase from *Bacillus amyloliquefaciens* for otherwise the same composition as **C5** and **C6** were tested as follows:

6 Plates each soiled with standardized starch soils or bleachable soils were washed in a Miele® G 575 dishwasher (detergent dose 20 g, universal program, water hardness 14-16°dH, operating temperature 55°C). The soil residue was gravimetrically determined and related to the starting value before washing (= 100%). The detergents according to the invention were significantly superior to the comparison detergents in terms of cleaning performance. The outcome was largely the same when the per acid in the detergents according to the invention was replaced by a conventional bleaching system of perborate/TAED.

## CLAIMS

1. An amylase-containing detergent, characterized in that it contains  $\alpha$ -amylase from *Bacillus amyloliquefaciens* and a percarboxylic acid in addition to typical ingredients compatible with such components.
- 5 2. A detergent as claimed in claim 1, characterized in that it contains amylase in quantities of 0.001 mg to 0.5 mg and more particularly in quantities of 0.02 mg to 0.3 mg per gram of the detergent as a whole.
3. A detergent as claimed in claim 1 or 2, characterized in that it contains 0.5% by weight to 20% by weight and more particularly 1% by
- 10 weight to 15% by weight of percarboxylic acid.
4. A detergent as claimed in any of claims 1 to 3, characterized in that the percarboxylic acid is a compound corresponding to general formula (I):



15 in which n is a number of 8 to 20 and more particularly 10 to 14.

5. A detergent as claimed in any of claims 1 to 3, characterized in that the percarboxylic acid is an amidoalkyl percarboxylic acid, more particularly a phthalimidoalkyl percarboxylic acid.
- 20 6. A detergent as claimed in claim 5, characterized in that the percarboxylic acid is phthalimidopercaproic acid.
7. A detergent as claimed in any of claims 1 to 6, characterized in that it contains 5% by weight to 50% by weight and more particularly 8% by weight to 30% by weight of surfactant.
- 25 8. A detergent as claimed in any of claims 1 to 6 for cleaning hard surfaces, more particularly for machine dishwashing, characterized in that it contains up to 10% by weight and more particularly 0.5% by weight to 3% by weight of surfactant.
9. The use of a combination of  $\alpha$ -amylase from *Bacillus*

amyloliquefaciens and percarboxylic acid for increasing the cleaning performance of detergents

10. The use claimed in claim 9, characterized in that the cleaning performance against starch-containing and/or colored soils is increased.

Replacement page

**CLAIMS**

1. An amylase-containing detergent, characterized in that it contains naturally occurring  $\alpha$ -amylase from *Bacillus amyloliquefaciens* and a percarboxylic acid in addition to typical ingredients compatible with such components.
2. A detergent as claimed in claim 1, characterized in that it contains amylase in quantities of 0.001 mg to 0.5 mg and more particularly in quantities of 0.02 mg to 0.3 mg per gram of the detergent as a whole.
- 10 3. A detergent as claimed in claim 1 or 2, characterized in that it contains 0.5% by weight to 20% by weight and more particularly 1% by weight to 15% by weight of percarboxylic acid.
4. A detergent as claimed in any of claims 1 to 3, characterized in that the percarboxylic acid is a compound corresponding to general formula (I):

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in which n is a number of 8 to 20 and more particularly 10 to 14.

5. A detergent as claimed in any of claims 1 to 3, characterized in that 20 the percarboxylic acid is an amidoalkyl percarboxylic acid, more particularly a phthalimidoalkyl percarboxylic acid.
6. A detergent as claimed in claim 5, characterized in that the percarboxylic acid is phthalimidopercaproic acid.
7. A detergent as claimed in any of claims 1 to 6, characterized in that 25 it contains 5% by weight to 50% by weight and more particularly 8% by weight to 30% by weight of surfactant.
8. A detergent as claimed in any of claims 1 to 6 for cleaning hard surfaces, more particularly for machine dishwashing, characterized in that it contains up to 10% by weight and more particularly 0.5% by weight to 3%

by weight of surfactant.

9. The use of a combination of naturally occurring  $\alpha$ -amylase from *Bacillus amyloliquefaciens* and percarboxylic acid for increasing the cleaning performance of detergents when used in water-containing  
5 washing/cleaning solutions
10. The use claimed in claim 9, characterized in that the cleaning performance against starch-containing and/or colored soils is increased.